Modification of a Carbon/Carbon Composite with a Thermosetting Resin Precursor as a Matrix by the Addition of Carbon Black

Tse-Hao Ko,[1] Wen-Shyong Kuo,[2] Wen-Teng Han,[1] Tzy-Chin Day[3]

[1]Department of Materials Science and Engineering, Feng Chia University, Taichung, Taiwan
[2]Department of Aeronautical Engineering, Feng Chia University, Taichung, Taiwan
[3]Union Chemical Laboratories, Industrial Technology Research, Hsinchu, Taiwan

ABSTRACT: Carbon/carbon composites were made through the pyrolysis of stabilized PAN felt and phenolic resin with the addition of 5 or 10 wt % carbon black to the matrix and then heat treatment at 600–2500°C. The effects of adding carbon black to the matrix precursor on the physical properties, microstructure, and mechanical properties of the resultant composites were investigated. Adding carbon black not only reduced the weight loss but also limited the shrinkage of the resultant composites. Adding carbon black also accelerated the formation of carbon basal planes in the matrix. At 2500°C, the crystalline stacking height in the composite with 10 wt % added carbon black was 200% greater than that with no additive. The flexural strength of the composite also increased from 15 to 42 MPa (almost 300%). © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 333–337, 2006

Key words: composites; mechanical properties; microstructure; resins

INTRODUCTION

Carbon/carbon (C/C) composites are excellent materials with a growing number of applications in the aerospace industry and other areas. C/C composites include high-tensile-strength or high-tensile-modulus carbon fibers to reinforce carbon matrices used in an inert atmospheres or used for short periods in oxidizing environments.[1] C/C composites, a family of compounds, range from randomly oriented chopped fibers to woven fabrics in a carbon matrix. Stabilized PAN felt has also been used as a reinforcement to reduce the cost of C/C composites in general applications.[2,3]

The matrix microstructure affects the overall performance and particularly the mechanical properties of a C/C composite. Phenolic resins serve as matrix precursors in C/C composites because they are relatively easy to use for impregnating fibers, and a large technology base exists for their use in conventional composites processing. Still, because of their plasticity and devolatilization during the early stages of heat treatment[2–8] and further shrinkage of the resins during pyrolysis, many pores and cracks can observed in composites after an initial heat treatment. Carbon yields from resins that cyclize, condense, and are readily converted to carbon normally range from 50 to 60 wt %.[1] The low density of the carbon that is formed limits the density of the final carbon composites. The initial void structure from the processing of phenolic resin-based C/C composites significantly influences their mechanical properties.[2–7]

Adding carbon black to coal–tar pitch increases the carbon yield and strength, improves the thermal properties, and reduces the porosity of pitch-based cokes.[9,10] In our previous work,[11] phenolic resins with 15 wt % carbon black had a 300% greater flexural strength and a 200% greater carbon yield than those produced from the original resin after heat treatment at 2500°C. The flexural strength of the C/C composite reinforced with stabilized PAN felt exceeded that of the composite reinforced with carbonized felt.[3] This work reports the influence of adding carbon black to the phenolic resin precursor on the physical and mechanical properties of the resultant C/C composites reinforced with stabilized PAN felt during pyrolysis.

EXPERIMENTAL

Resole-type phenol–formaldehyde resin was supplied by Chang Chun Petrochemical Industries (Taiwan) in a solution with a 60 wt % solid content; N-660 carbon black was purchased from Korea Steel Chemical Co.,
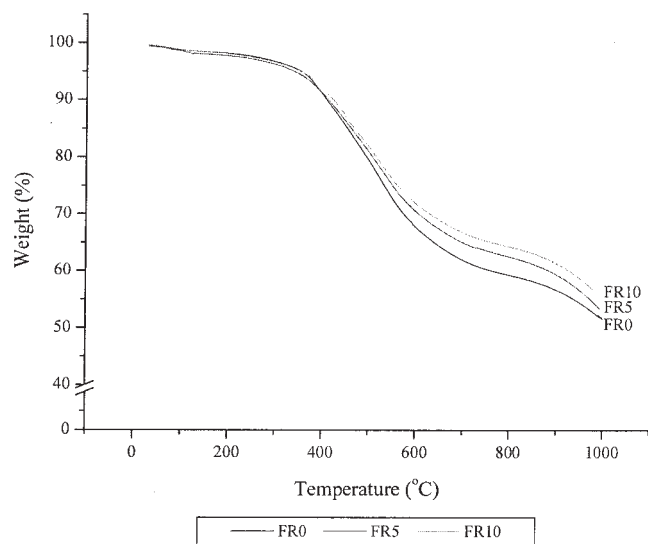

Figure 1 TGA curves of specimen FR0 (original composite), specimen FR5 (composite with 5 wt % carbon black added), and specimen FR10 (composite with 10 wt % carbon black added).

Ltd. The matrix was prepared by the addition of 5 or 10 wt % carbon black to the resin. The resin and carbon black were well mixed; C/C composites were made with stabilized PAN felt (Toho Rayon Co., Ltd., Japan) and resol-type phenol–formaldehyde resin. The polymer composites were cured at 80°C for several minutes and subsequently hot-pressed at 30 kg/cm² and 120°C for 30 min and at 160°C for 10 min. The cured composites were cut to an appropriate size, and the samples were pyrolyzed at a heating rate of 0.5°C/min to 600, 1000, 1800, or 2500°C. The heat-treated composites with 0, 5, and 10 wt % carbon black added were labeled FR0, FR5, and FR10, respectively.

The flexural strength of the composites was determined by the three-point-bending method according to ASTM D 790. The open porosity of the composites was measured according to ASTM D 570. The real density was measured with an AccuPyc 1330 pycnometer in helium.

A Diano model 8536 X-ray diffractometer, providing Ni-filtered Cu Kα radiation, was used to measure the crystallinity-related characteristics of the samples. The step-scan method was used to determine the d-spacing and stacking size [i.e., the stacking height of the layer planes (L_c)]. The step interval was set at 0.02°. The d-spacing and L_c were calculated with eqs. (1) (the Bragg equation) and (2) (the Scherrer equation), respectively:

$$n\lambda = 2d \sin \theta \quad (1)$$

$$L_c(hkl) \text{ (nm)} = K\lambda/B \cos \theta \quad (2)$$

where λ is 0.1542 nm, K is the apparatus constant (1.0), and B is the half-value width (rad) of the curve of the X-ray diffraction intensity versus 2θ.

RESULTS AND DISCUSSION

Weight loss and shrinkage

Figure 1 shows the thermogravimetric analysis (TGA) results. Pyrolysis removed non-carbon elements from the cured composite as volatiles.[12,13] When all the samples were heat-treated in N_2 up to 1000°C under TGA with the temperature increasing at a rate of 10°C/min, the weight loss of FR0 was 48 wt %, that of FR5 was 47 wt %, and that of FR10 was 44 wt %. Figure 1 reveals that adding carbon black to the matrix reduced the weight loss and increased the carbon yield, a higher carbon black content corresponding to a lower weight loss of the composites.

Figure 2 presents the variation of the weight loss of the composites during the heat treatment. The weight loss was determined from the change in the weight between the postcured and heat-treated samples. The weight loss was significant below 600°C and almost complete above 1000°C. Below 600°C, the matrix could be heated slowly to form glassy carbon products with appropriate mechanical properties. At 2500°C, the weight losses of samples FR0, FR5, and FR10 were approximately 42, 37, and 35 wt %, respectively.

Like the weight loss, linear shrinkage occurred continuously up to 1000°C, declining as the temperature further increased above 1000°C, as shown in Figure 3. Shrinkage above 1000°C was caused primarily by a rearrangement of the carbon structure, as evidenced by the very small weight losses above 1000°C. The weight loss of the composites made with carbon black was lower than that of the composites without carbon black addition during the heat treatment. The composite with added carbon black also experienced limited shrinkage during the heat treatment.
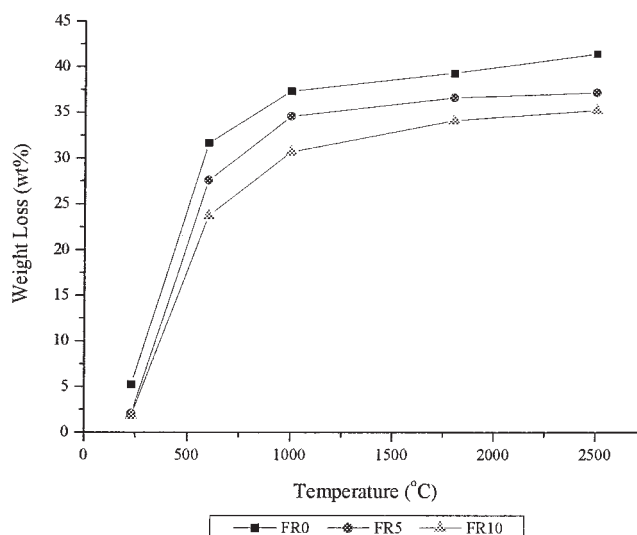

Figure 2 Variation of the weight loss of the composite and composites with carbon black added during pyrolysis.
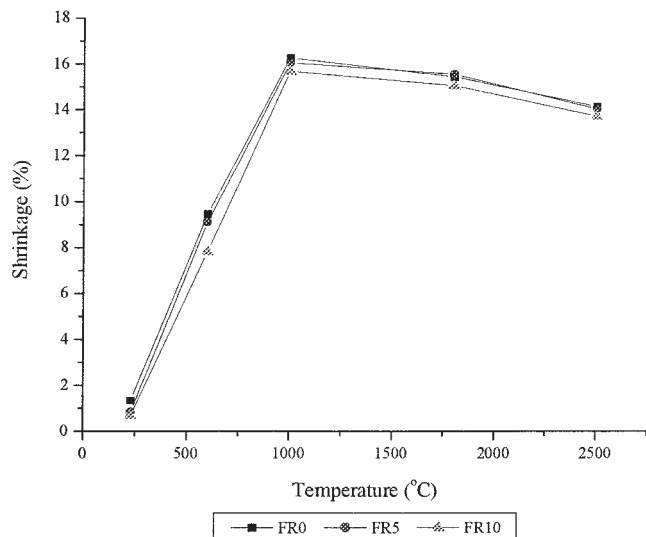
Figure 3 Variation of the linear shrinkage of the composite and composites with carbon black added during pyrolysis.

Figure 5 Variation of the real density of the composite and composites with carbon black added during pyrolysis.

Density and porosity

Figures 4 and 5 show the variation in the open porosity and bulk density of the composites during the heat treatment. Two factors influenced the bulk density of the carbonized samples: the rate of pore formation and the degree of chemical densification caused by the change in the chemical structure of the fiber, matrix, and carbon black during pyrolysis. During the early stage of pyrolysis, evolved gases created many pores in the composites. The chemical structure of the fiber and matrix also changed into a carbon structure, and this meant that the bulk density increased with the temperature, maximizing at 1000°C. Above 1000°C,
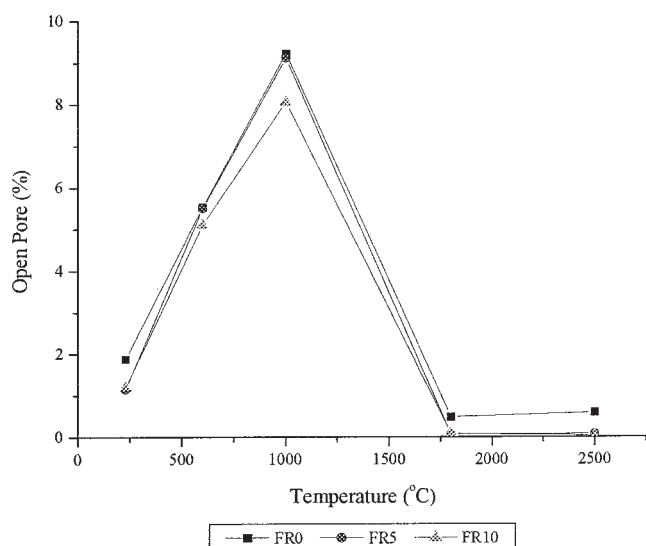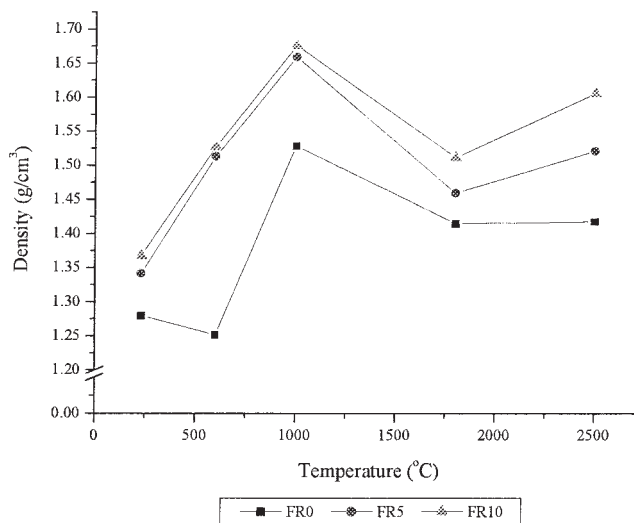
the changed chemical structure reduced the number of open pores, which closed as the carbon structure was rearranged.[3,11,14–19] These reactions reduced the density.

Around 1800°C, very small increases in the number of open pores emanated chiefly from the rearrangement of the chemical structures and formation of the graphite structure. These reactions increased the density. Figure 5 shows that the density of the composite with carbon black was greater than that of the composite without it at 2500°C. At this temperature, the densities of C/C composites FR0, FR5, and FR10 were 1.42, 1.52, and 1.61 g/cm^3, respectively; the density of the composite with 10 wt % added carbon black was 14% higher than the density of that without it.

X-ray diffractometry

Figure 6 shows X-ray diffraction patterns of the original composites and those with 10 wt % carbon black added during pyrolysis. The composites cured at 230°C, FR0-230 and FR10-230, show two broad peaks at $2\theta \approx 10°$ and $2\theta \approx 19°$, respectively. These peaks are related to adjacent chains of the linear polymer.[17] Figure 6(b) shows cured composite FR10-230 yielding another peak at $2\theta \approx 25°$, caused by the addition of 10 wt % carbon black. The diffraction profiles of the polymer structure include maxima at $2\theta \approx 10°$ and $2\theta \approx 19°$, becoming broader and less intense with rising temperature.

When a composite was heat-treated at 600°C, a new peak at $2\theta \approx 22.5°$ was found because a carbonlike structure formed from the polymer structure, as shown in Figure 6(a). The peaks at $2\theta \approx 22.5°$ and $2\theta \approx 25°$ [Fig. 6(b)] correspond to (002) reflections of the carbon material. The peak at $2\theta \approx 22.5°$ shifted to 2θ

Figure 4 Variation of the open pores of the composite and composites with carbon black added during pyrolysis.
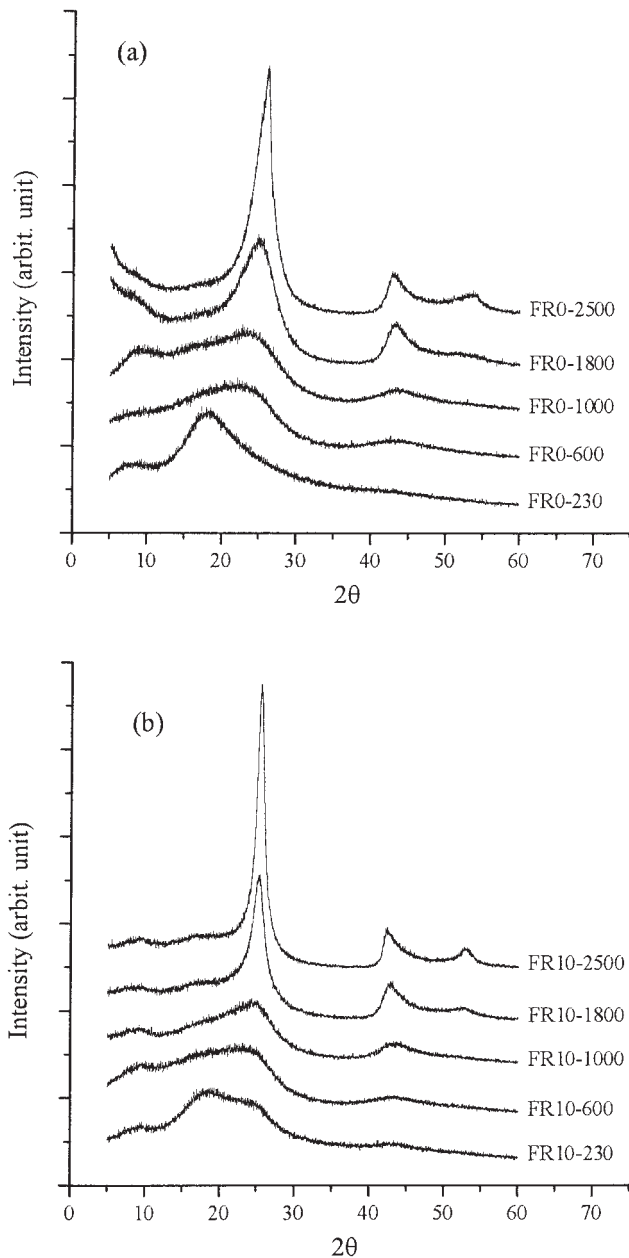
Figure 6 Wide-angle diffraction patterns of the composites during the heat treatment: (a) original composite and (b) composite with 10 wt % carbon black added.

≈ 24° at 1000°C by a transformation from the carbon-like structure to a turbostractic carbon structure. The intensity of this peak increased with the heat-treatment temperature.

When cured composites were carbonized at 600°C, a new broad peak appeared at between 2θ values of 40 and 50°. This peak was attributed to (10l) reflections of the turbostractic carbon structure; its intensity increased with the temperature. The peak of the composite with 10 wt % added carbon black was clearer than that obtained with none added. This finding demonstrates how composites with added carbon

black are more crystalline than those without added carbon black. Above 1800°C, the (10l) peak of the composites with 10 wt % added carbon black (FR10-1800 and FR10-2500), like the peak at 25°, was higher and narrower than that of other composites without added carbon black. This result indicates composites with added carbon black have greater L_c.

Figure 7 plots the variation of L_c of the composites during pyrolysis: L_c values climbed with the temperature. Below 1000°C, L_c rose very slowly; this indicated that the carbon structure formed slowly. At this stage, the structure was disordered. L_c increased very rapidly with the temperature above 1000°C because a turbostractic carbon structure formed in the fibers and matrix.

The composites with added carbon black had higher L_c values than those with none added during pyrolysis. At 2500°C, the L_c values of FR0, FR5, and FR10 were 3.9, 6.9, and 7.7 nm, respectively. L_c of the composite with 10 wt % added carbon black was double that of the composite without the carbon black additive.

Mechanical properties

Figure 8 plots the effects of adding carbon black on the flexural strength of the composites during pyrolysis. The formation of strong bonding between the fibers and matrix enabled the cracks in the matrix to cut the fibers easily, so that their strength was low.[11] Adding carbon black increased the flexural strength of the composites during pyrolysis. The fracture pattern of the composites showed a catastrophic fracture with a smooth fracture surface. Although adding 10 wt % carbon black im-
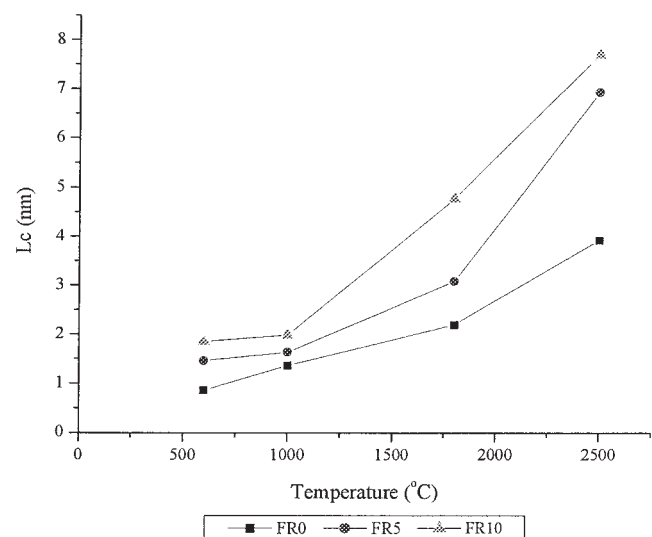

Figure 7 Variation of L_c of the composite and composites with carbon black added during pyrolysis.
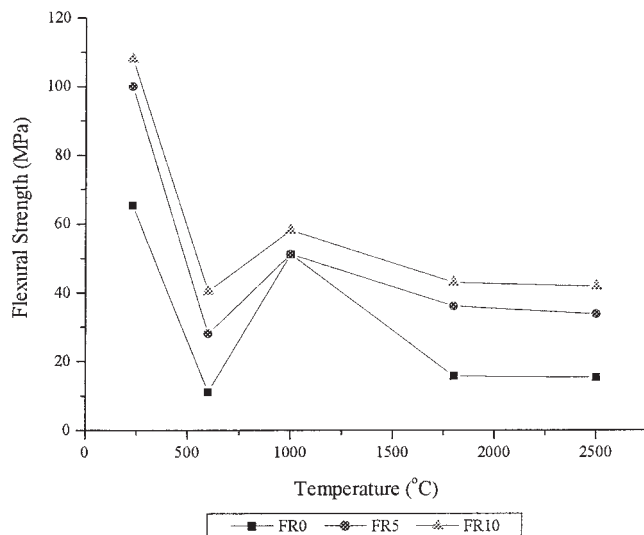
Figure 8 Variation of the flexural strength of the composite and composites with carbon black added during pyrolysis.

proved the flexural strength of the composites, the failure remained of the catastrophic type.

This work indicates that adding carbon black encourages the formation of carbon crystals in the matrix, increasing the density and reducing the porosity. Strong bonds that formed between the carbon black and matrix promoted the formation of an anisotropic carbon structure around the carbon black during pyrolysis. These structures caused L_c of the composites with added carbon black to exceed that of composites without it. Ordered areas were formed around the carbon black, which was uniformly distributed; cracks branched from these ordered structures. The strong bonding between the matrix and carbon black limited the shrinkage and formation of pores in the matrix, increasing the strength. However, ordered structures formed around the carbon black. The reactions boosted the flexural strength of the C/C composite with carbon black added. At 2500°C, the flexural strength of composites FR0, FR5, and FR10 were 15.5, 34.0, and 42.0 MPa, respectively. The flexural strength of the composite with 10 wt % added carbon black was almost 300% higher than the strength of the composite without it.

In this work, stabilized PAN felt was used, because of its low cost, for concocting C/C composites with a wide range of applications. Adding carbon black to the matrix improved the mechanical and physical properties of the resultant C/C composite, yet commercial applications need to be further investigated.

CONCLUSIONS

As a filler, 5–10 wt % carbon black was added to a matrix of a stabilized PAN felt/thermosetting resin to develop C/C composites with a wide range of applications. The formation of strong bonds between the added carbon black and matrix caused the composites to exhibit lower weight loss and limit shrinkage, plus higher density and suppressed formation of pores. Adding composite carbon black to the matrix promoted the growth of crystalline carbon around the carbon black. This reaction promoted the formation of crystalline carbon, so the composites with added carbon black had greater L_c values than those without added carbon black.

At 2500°C, L_c of the crystals of the composite with 10 wt % added carbon black was improved by 200% over that of the C/C composite without it. The formation of an ordered structure around carbon black and the suppressed formation of large pores in the matrix gave the C/C composite greater flexural strength than that of the composite with none added. At 2500°C, the flexural strength of composites FR0, FR5, and FR10 was 15.5, 34.0, and 42.0 MPa, respectively. The flexural strength of the composite with 10 wt % added carbon black in its matrix increased by 300% in comparison with that of the composite with no added carbon black.

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